Modeling and Characterization of a Graphite Nanoplatelet/Epoxy Composite

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ABSTRACT

A micromechanical modeling procedure is developed to predict the viscoelastic properties of a graphite nanoplatelet/epoxy composite as a function of volume fraction and nanoplatelet diameter. The predicted storage and loss moduli from the model are compared to measured values from the same material using Dynamical Mechanical Analysis, nanoindentation, and tensile tests. In most cases, the model and experiments indicate that for increasing volume fractions of nanoplatelets, both the storage and loss moduli increase. Also, in most cases, the model and experiments indicate that as the nanoplatelet diameter is increased, the storage and loss moduli decrease and increase, respectively.

INTRODUCTION

In recent years, nanostructured materials have spurred considerable interest in the materials research community partly because of their potential for large gains in mechanical properties relative to current materials used for aerospace applications. This is particularly important in the design and development of Unmanned Aerial Vehicles (UAVs), in which the primary requirements are long-duration, high-altitude flights. Graphite nanoplatelet/polymer composites have been recently developed for use as a low-cost, lightweight materials with properties potentially superior to those of pure polymers. In order to facilitate the development of these materials for UAVs, modeling and characterization procedures must be developed over the nano- to macro-length scales.

Recently, experiments were conducted to determine the viscoelastic properties of a series of graphite nanoplatelet/epoxy composite specimens that were fabricated at Michigan State University [1]. The specimens contained varying amounts of nanoplatelet volume fractions, sizes, and preparations. The experimental tests included nanoindentation, Dynamical Mechanical Analysis (DMA), and tensile testing. Since these tests were conducted over a wide range of length scales, the viscoelastic properties for each test must be interpreted based on the relative scale of the test method and scale of the heterogeneity of the material. However, the interpretation and comparison of the experimental data is difficult without the knowledge of the expected viscoelastic properties.

In the current paper, a modeling procedure has been developed to facilitate the interpretation of the experimental data. A brief summary of the material and test methods is followed by a detailed explanation of the modeling procedure. The predicted viscoelastic properties from the modeling are compared to the experimentally obtained properties.

MATERIALS

In this study, the viscoelastic properties of four graphite nanoplatelet/epoxy composite materials were examined. The four materials had two different average sizes of graphite nanoplatelets, 1 and 15 μm diameters, for two different nanoplatelet volume fractions, 0.5% and 3.0%. The test specimens were fabricated at Michigan State University, and further details on the material fabrication and characterization can be found elsewhere [2]. Fig. 1 shows an Atomic Force Microscope (AFM) image of the 1 μm-reinforced composite with a nanoplatelet volume fraction of 3%. From Fig. 1 it is clear that the nanoplatelets are well dispersed and randomly oriented in the epoxy matrix.

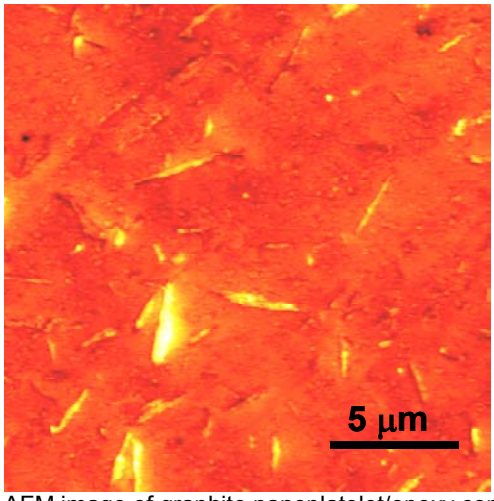

Fig. 1. AFM image of graphite nanoplatelet/epoxy composite

TEST METHODS

Three test methods were used to determine the mechanical properties of the four composite materials, Dynamical Mechanical Analysis (DMA), quasi-static tensile testing, and nanoindentation. In DMA testing, an oscillatory force is applied onto a bulk sample and the resultant dynamic modulus is measured. These tests were standard tests based on well-established procedures [3, 4]. Quasi-static tensile tests were also performed on bulk samples. Using a standard tensile-testing machine and strain-measuring equipment, the Young's modulus and Poisson's ratio were determined for the four composite materials. Nanoindentation tests were performed on samples of the four materials using a previously established procedure [5]. In the nanoindentation procedure, a nanometer-sized tip was indented up to 2.0 μm into the specimen. A relatively small oscillatory displacement was superimposed onto the overall tip displacement, and the resulting dynamic modulus was measured. Further details on the application of these test methods to the four composite materials considered in the study may be found elsewhere [1].

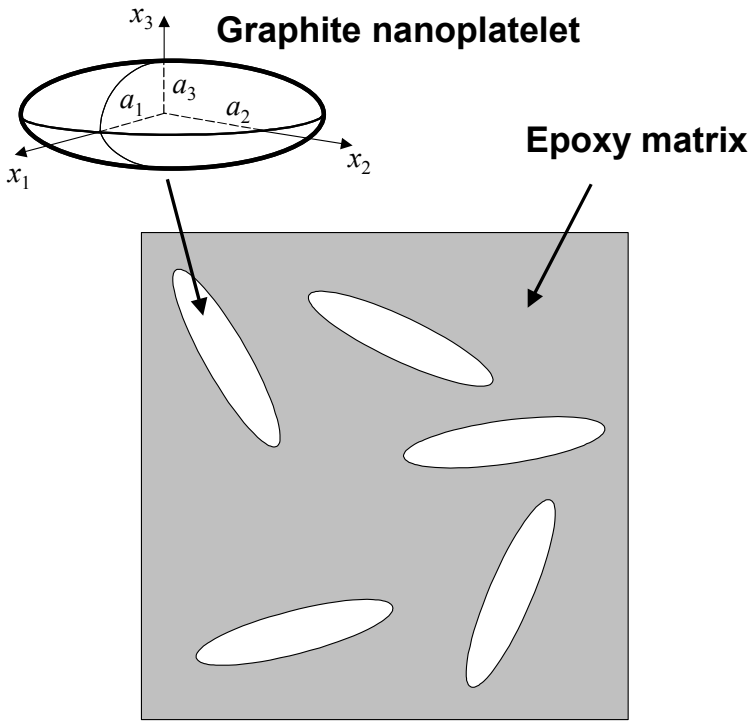

Fig. 2. Micromechanical modeling of graphite nanoplatelet/epoxy composite

MICROMECHANICS MODEL

The viscoelastic properties of the four composite materials were predicted by using a micromechanics model that incorporated the viscoelastic properties of the graphite and epoxy constituents. The micromechanics-based Mori-Tanaka method [6, 7] was used in conjunction with the elastic-viscoelastic correspondence principle [8]. To implement this model for the graphite nanoplatelet/epoxy composite, it was assumed that the nanoplatelets were randomly-oriented oblate-spheroids that were perfectly bonded to the surrounding matrix (Fig. 2). In this case, the composite complex modulus is

$$\mathbf{C}^* = \left(c_m \mathbf{C}_m^* + c_p \left\langle \mathbf{C}_p^* \mathbf{A}_p^* \right\rangle\right)\left(c_m \mathbf{I} + c_p \left\langle \mathbf{A}_p^* \right\rangle\right)^{-1} \tag{1}$$

where c_p and c_m are the nanoplatelet and matrix volume fractions, respectively, $\mathbf{C}_p^*$ and $\mathbf{C}_m^*$ are the complex stiffness tensors of the nanoplatelets and matrix, respectively, $\mathbf{I}$ is the identity tensor, the angle-brackets indicate a nanoplatelet-orientation average, and $\mathbf{A}_p^*$ is the complex dilute strain-concentration tensor of the nanoplatelets. The complex quantities in Eqn. (1) and throughout this paper can be expressed in terms of storage (time-independent) and loss (time-dependent) components. For example, the complex stiffness tensor of the composite is

$$\mathbf{C}^* = \mathbf{C}' + i\mathbf{C}'' \tag{2}$$

where $\mathbf{C}'$ and $\mathbf{C}''$ are the composite storage and loss stiffness tensors, respectively. The complex dilute strain-concentration tensor in Eqn. (1) is

$$\mathbf{A}_p^* = \left[\mathbf{I} + \mathbf{S}^* \left(\mathbf{C}_m^*\right)^{-1} \left(\mathbf{C}_p^* - \mathbf{C}_m^*\right)\right]^{-1} \tag{3}$$

where $\mathbf{S}^*$ is the complex Eshelby tensor. The complex Eshelby tensor is determined by applying the elastic-viscoelastic correspondence principle to the Eshelby tensor for elastic composites [9, 10], which yields

$$\begin{aligned}
S_{1111}^* &= \frac{3}{8\pi\left(1-\nu^*\right)} a_1^2 J_{11} + \frac{1-2\nu^*}{8\pi\left(1-\nu^*\right)} J_1 \\
S_{1122}^* &= \frac{1}{8\pi\left(1-\nu^*\right)} a_2^2 J_{12} - \frac{1-2\nu^*}{8\pi\left(1-\nu^*\right)} J_1 \\
S_{1133}^* &= \frac{1}{8\pi\left(1-\nu^*\right)} a_3^2 J_{13} - \frac{1-2\nu^*}{8\pi\left(1-\nu^*\right)} J_1 \\
S_{1212}^* &= \frac{a_1^2 + a_2^2}{16\pi\left(1-\nu^*\right)} J_{12} + \frac{1-2\nu^*}{16\pi\left(1-\nu^*\right)} \left(J_1 + J_2\right)
\end{aligned} \tag{4}$$

where ν^* is the complex Poisson's ratio; $a_1 = a_2 > a_3$ are the principle half-axes of the oblate spheroid inclusion (Fig. 2); $S_{ijkl}^* = S_{jikl}^* = S_{ijlk}^*$; all other non-zero components are obtained by cyclic permutation of (1,2,3); the components which cannot be obtained by the cyclic permutation are zero; and

$$\begin{aligned}
J_1 &= J_2 = \frac{2\pi a_1^2 a_3}{\left(a_1^2 - a_3^2\right)^{3/2}} \left[\cos^{-1}\left(\frac{a_3}{a_1}\right) - \frac{a_3}{a_1}\left(1 - \frac{a_3^2}{a_1^2}\right)^{1/2}\right] \\
J_3 &= 4\pi - 2J_1 \\
J_{11} &= J_{22} = J_{12} = \frac{\pi}{a_1^2} - \frac{J_1 - J_3}{4\left(a_3^2 - a_1^2\right)} \\
J_{13} &= J_{23} = \frac{J_1 - J_3}{a_3^2 - a_1^2} \\
J_{33} &= \frac{1}{3}\left(\frac{4\pi}{a_3^2} - 2J_{13}\right)
\end{aligned} \tag{5}$$

For three-dimensional randomly-oriented nanoplatelets, the orientation average of a tensor, $\mathbf{T}$, is

$$\langle \mathbf{T} \rangle = \langle T_{ijkl} \rangle = \left(\kappa - \frac{2}{3}\mu \right)\left(\delta_{ij}\delta_{kl} \right) + \mu\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} \right) \tag{6}$$

where i,j,k,l = 1,2,3; the indicial summation convention is used; δ_{ij} is the Kronecker delta; and

$$\begin{aligned} \kappa &= \frac{1}{9} A_{iijj} \\ \mu &= \frac{1}{10}\left(A_{ijij} - \frac{1}{3} A_{iijj} \right) \end{aligned} \tag{7}$$

Therefore, from Eqns. (6) and (7), $\langle \mathbf{T} \rangle$ is isotropic.

The properties of the constituent materials used in the modeling are shown in Table 1. For this study, it was assumed that the graphite nanoplatelets were linear-elastic, with the classic transverse-isotropic graphite mechanical properties being used [11], where the x_3 axis is perpendicular to the graphene plane. The storage and loss moduli, E' and E'', respectively, of the epoxy material were determined via DMA testing [1]. It was assumed that the storage shear modulus, G', was equal to the static shear modulus, which was computed using the Young's modulus and Poisson's ratio determined via the quasi-static tensile testing [1]. The loss shear modulus, G'', was determined using [12]

$$tan\,\delta = \frac{E''}{E'} = \frac{G''}{G'} \tag{8}$$

With these assumptions, it was possible to uniquely determine all of the components of the complex stiffness tensors of the nanoplatelets and polymer using the elastic-viscoelastic correspondence principle.

Table 1. Viscoelastic properties of constituent materials in GPa

	Graphite	Epoxy
C_{11}^*	106.00	$4.30 + 0.16i$
C_{12}^*	18.00	$2.12 + 0.08i$
C_{13}^*	1.50	$2.12 + 0.08i$
C_{33}^*	3.65	$4.30 + 0.16i$
C_{44}^*	0.45	$1.09 + 0.04i$

For the complex Eshelby tensor, the complex properties of the epoxy and the shape of the nanoplatelets were used in Eqns. (4) and (5). From AFM images of the material, such as that shown in Fig. 1, it was determined that the graphite nanoplatelets had a thickness of about 0.5 μm for the 1 μm nanoplatelets and 1 μm for the 15 μm nanoplatelets [1].

It is noted that even though it has been previously shown that the mechanical properties of composites with nanometer-sized reinforcement must be modeled using an equivalent-continuum modeling approach [13, 14], the smallest dimension of the nanoplatelet is 0.5 μm, which is large enough to be modeled directly using micromechanics, as demonstrated previously [15].

RESULTS

The storage moduli of the four composite materials measured in the DMA and nanoindentation experiments and predicted with the model are shown in Fig. 3. In addition, the Young's moduli of three of the composite materials as measured via the tensile tests are shown in Fig. 3. The loss moduli of the composite materials measured through DMA and nanoindentation

experiments and predicted by the model are shown in Fig. 4. The error bars shown for the experimental data in Figs. 3 and 4 are the standard error as measured through repeat tests.

It is evident in Fig. 3 that there is reasonable agreement between all of the experimental tests. Except for the 0.5% volume fraction with 1μm nanoplatelets, the DMA values of storage modulus are higher than the nanoindentation values for each material. There is no clear trend for the three tensile test values. Further analysis of the data leads to two important points. First, for all three experimental sets of data, the storage modulus (or Young's modulus for the tensile tests) increases with an increasing nanoplatelet volume fraction, as expected. The model confirms this trend. Second, for the nanoindentation and tensile test data, the storage (or Young's) modulus increases with the decreasing nanoplatelet size. The model confirms this trend, even though the DMA data does not follow this trend. Therefore, decreasing the diameter (while decreasing the thickness by a lesser amount), as done in the modeling, results in increasing storage (or Young's) moduli.

In Fig. 4, it is clear that the loss moduli measured with nanoindentation are at least 50% higher than those measured with the DMA for the four composite materials, and that the model shows much better agreement with the DMA data than for the nanoindentation data. The latter trend is expected because the model used the epoxy viscoelastic properties obtained from DMA tests. While the experimental data show an increase in loss modulus with increased nanoplatelet volume fraction, the model does not exhibit this trend with the 1 μm nanoplatelets. Furthermore, both experiments and model indicate an increase in loss modulus with increased nanoplatelet diameter.

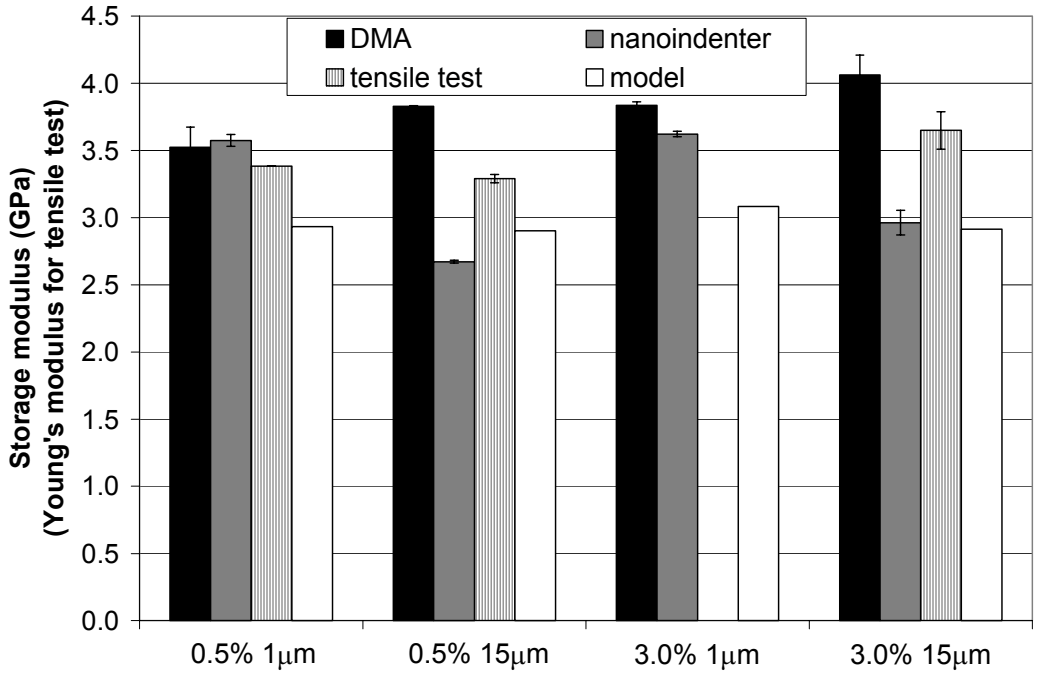

Fig. 3. Storage moduli for graphite nanoplatelet/epoxy composites

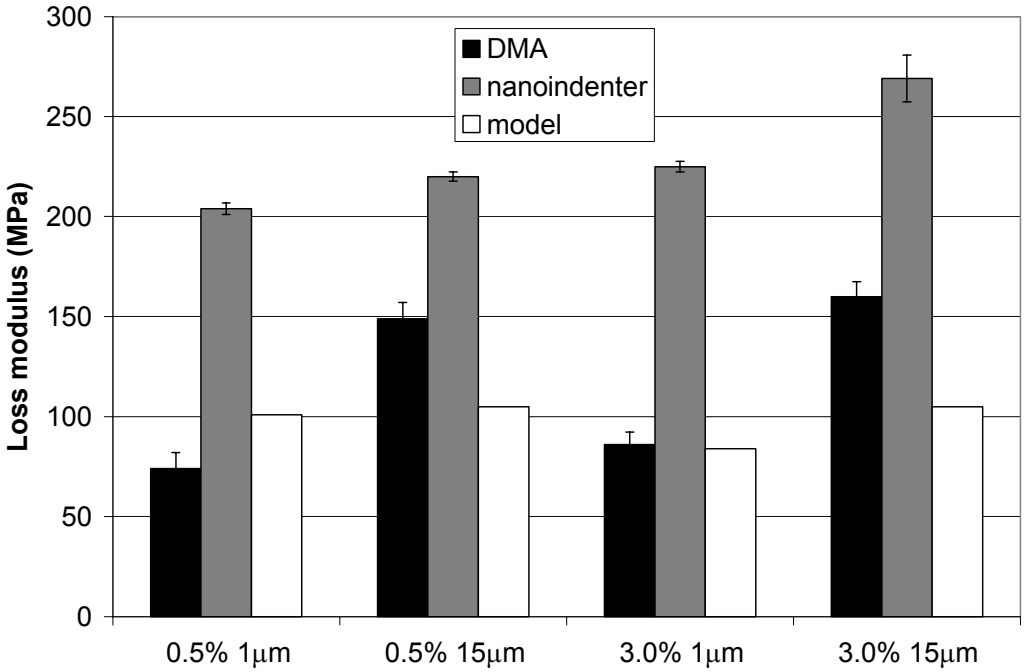

Fig. 4. Loss moduli for graphite nanoplatelet/epoxy composites

SUMMARY

In this study, a micromechanical modeling procedure was developed to predict the viscoelastic properties of graphite nanoplatelet/epoxy composites as a function of volume fraction and nanoplatelet diameter. The objective of the model was to compare the predicted with the experimentally measured viscoelastic properties of this material from DMA, nanoindentation, and tensile tests, and thus facilitate the interpretation of the experimental data.

The results of the modeling and all three sets of experiments indicate that for increasing volume fraction of nanoplatelets, the storage modulus increases. Even though an increase in nanoplatelet volume fraction leads to higher values of loss modulus in the experiments, the model does not show this trend. Except for the DMA data, the tests and model indicate that the storage modulus increases with decreasing nanoplatelet. For the same decrease in nanoplatelet diameter, the modeling and experiments both show a decrease in loss modulus of the composite.

REFERENCES

1. Chasiotis, I.; Chen, Q.; Odegard, G.M., and Drzal, L.: Multiscale Experiments on Graphite Nanoplatelet/Epoxy Composites. *SEM X International Congress and Exposition on Experimental and Applied Mechanics*. Costa Mesa, CA; Society of Experimental Mechanics, 2004.
2. Fukushima, H. and Drzal, L.: Graphite Nanoplatelets as Reinforcements for Polymers: Structural and Electrical Properties. *17th Annual American Society for Composites Technical Conference*. West Lafayette, IN; 2002.
3. Menard, K.P.: *Dynamic Mechanical Analysis: A Practical Introduction*. Boca Raton, FL: CRC Press, 1999.
4. Kampf, G.: *Characterization of Plastics by Physical Methods: Experimental Techniques and Practical Application*. New York: Hanser Publishers, 1986.
5. Odegard, G.M.; Bandorawalla, T.; Herring, H.M., and Gates, T.S.: Characterization of Viscoelastic Properties of Polymeric Materials Through Nanoindentation. *2003 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*. Charlotte, NC; Society of Experimental Mechanics, 2003.
6. Mori, T. and Tanaka, K.: Average Stress in Matrix and Average Elastic Energy of Materials with Misfitting Inclusions. *Acta Metallurgica*. Vol. 21, 1973, pp. 571-574.
7. Benveniste, Y.: A New Approach to the Application of Mori-Tanaka's Theory in Composite Materials. *Mechanics of Materials*. Vol. 6, 1987, pp. 147-157.
8. Brinson, L.C. and Lin, W.S.: Comparison of Micromechanics Methods for Effective Properties of Multiphase Viscoelastic Composites. *Composite Structures*. Vol. 41, 1998, pp. 353-367.
9. Eshelby, J.D.: The Determination of the Elastic Field of an Ellipsoidal Inclusion, and Related Problems. *Proceedings of the Royal Society of London, Series A*. Vol. 241, 1957, pp. 376-396.
10. Mura, T.: *Micromechanics of Defects in Solids*. The Hague: Martinus Nijhoff, 1982.

11. Kelly, B.T.: *Physics of Graphite*. Essex, England: Applied Science Publishers LTD, 1981.
12. Ferry, J.D.: *Viscoelastic Properties of Polymers*. New York: John Wiley & Sons, Inc., 1980.
13. Odegard, G.M.; Gates, T.S.; Wise, K.E.; Park, C., and Siochi, E.J.: Constitutive Modeling of Nanotube-Reinforced Polymer Composites. *Composites Science and Technology*. Vol. 63, 2003, pp. 1671-1687.
14. Odegard, G.M.; Frankland, S.J.V., and Gates, T.S.: The Effect of Chemical Functionalization on Mechanical Properties of Nanotube/Polymer Composites. *44th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*. Norfolk, VA; 2003.
15. Odegard, G.M.; Clancy, T.C., and Gates, T.S.: Constitutive Modeling of Nanoparticle-Reinforced Polyimides. *2003 ASME International Mechanical Engineering Congress and Exposition*. Washington, DC; 2003.